REACTIVITY AND REACTIONS OF SOME AUSTRALIAN BROWN COALS

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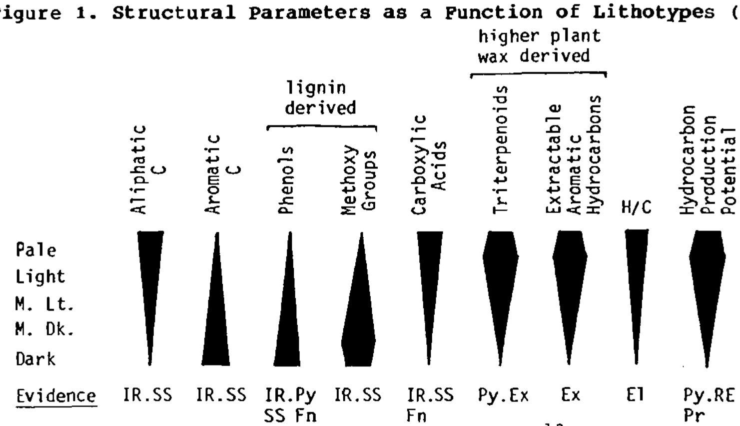
The brown coal seams situated in the Latrobe Valley, Victoria, Australia are known to derive predominantly from a higher plant input (1) and represent approximately 25% of the world's supply of brown coal (2). The coals occur in five major lithotypes whose chemical composition vary from one another as illustrated in Figure 1.

Figure 1. Structural Parameters as a Function of Lithotypes (3)



IR = Infrared; Py = Pyrolysis/GC; SS = Solid State C^{13}-NMR;
Fn = Functional group analyses; Ex = Extractable components;
El = Elemental analyses; RE = Rock-Eval; Pr = Proximate analyses.

The high water content of Victorian brown coals at approximately 60% is characteristic of these coals but its removal has proved economically disadvantageous. It has recently proved possible, however, to reduce the water content to approximately 10% in a process of densification (4) which is under patent protection (5). The densified brown coal (DBC) produced compares favourably in its Net Wet Specific Energy with a black coal and retains all the other gross characteristics of the raw brown coal.

Densification can also be regarded as a dewatering process. The scheme of production of a DBC is shown in Figure 2 (4) whilst Figure 3 illustrates the loss of moisture with time at ambient temperature and relative humidity. This release of water from the pores of the coal whilst initiated by the attritioning procedure is accompanied by chemical cross-linking reactions and the main thrust of this paper is to explore the chemical aspects of densification.

Table 1. Comparison of Black and Brown Coals with Densified Brown Coal from the Morwell (Vic) Seam.

	Brown coal Morwell, Vic.	Black coal Tarong, Qld.	Densified brown coal
Moisture	59% wb	5.2% adb	15.9% adb
Volatile matter	49.2% db	29.7% db	48.9% db
Fixed carbon	48.8% db	40.9% db	49.1% db
Ash	2.4% db	29.4% db	2.4% db
Total suphur	0.3% db	0.42% db	0.3% db
GSE	27.2 MJ/kg daf	31.98 MJ/kg daf	27.2 MJ/kg daf
NWSE	8.4 MJ/kg	21.3 MJ/kg adb	22.0 MJ/kg adb
Bulk density	1130 kg/m^3		1200-1700 kg/m^3

wb - wet basis. adb - air dry basis. db - dry basis. daf - dry ash free. GSE - gross specific energy on a dry ash free basis. NWSE - net wet specific energy.

Victorian brown coals are not only chemically complex in components but are physically porous. Kneading will reduce the particle size of the coal and liberate water from the pore structure forming a slurry or paste. Figure 4 illustrates the effects of kneading on the changes in diameter of 10mm pellets on drying. The shinkage observed is a consequence of loss of water content but also of the development of considerable strength in the pellets as Figure 5 illustrates. Morwell DBC pellets can sustain a load of 280kg at a crush strength of 35MPa. There is a marked difference between the crush strengths developed in DBC from Loy Yang and Morwell coals (Fig. 5) although particle size is the same for both coals. This difference is reflected also in porosities after densification (37% volume porosity for Loy Yang coal versus 14.6% for Morwell) which appear to be the inverse of crush strengths (5.7 for Loy Yang versus 18.5 MPa for Morwell). Pellet shrinkage and the development of crush strength with time can be interpreted as chemical cross-linking reactions drawing microdomains together and in the process excluding water and densifying. Strong pellets may develop cracks on the surface and the crush strengths measured reflect the point of greatest weakness. The shattered fragments retain their strength however.

In seeking to explain these physical changes in terms of chemical reactions it is unlikely that only one class of reactions is involved; rather a range of chemical interactions must be considered. It is known that Victorian brown coals do contain stable free radicals and that as the coal particles are brought closer together by the physical kneading, radical couplings could occur which include cross-linking reactions. We have often noted that a small crush strength maximum develops in the early stages of attritioning which probably occurs as a result of this type of bond formation. Additional forms of bonding would involve ionic reactions, the most likely centres of reaction being carboxyl groups, phenols and activated aromatic systems. The strong pH control of development of crush strength suggests that ionic reactions are the probable cross-linking reactions. Figures 3 - 5 show how densification is coal dependent, but Figure 1 illustrates how compositional differences will also be lithotype-dependent so that the averaged reactivities of ROM coals integrate several variables.

A dominating parameter in the control of crush strength (σ_c) of DBC pellets is the pH of the raw coal (Figure 6). Coals have a natural pH which may vary depending upon storage time and exposure to air. The more acidic the coal, the smaller the crush strength of the DBC. However, basic additives can raise the crush strengths as illustrated for $NaHCO_3$ as an additive to Loy Yang coal (Figure 6). Loy Yang is a naturally acidic coal (pH 3.2) but shows a dramatic change in σ_c with increase of pH. NaOH, a strong base, when used as an additive gives a DBC showing a maximum σ_c at approximately pH 6. This is close to the pH (5.3) determined for ROM Morwell coal and thus explains why a strong base additive does not usefully improve its performance during densification.

Clearly, (i) the O-/OH and COO-/COOH ratios in the brown coals, (ii) the absolute abundances of these fuctional groups, and (iii) their sensitivity to pH are major controlling factors in determining crush strength. In turn these oxygen functional groups can be expected to interact by substituting in activated aromatic systems in the coal. Again, pH will be important in facilitating such interactions. The molecular complexity of the likely reactions will mean that at best a range only of reactions and reactivities will be observed. Given that oxygen functionalities can be expected to play a significant role in densification, one probe would be to sequester acidic hydroxyl groups and observe the effect on crush strengths on densification.

Methylation of brown coals using tetrabutylammonium hydroxide/methyliodide as the methylating agent has an advantage that it swells the coal and utilises the water already inherent in the coal. Methylation affects densification in two ways: first, the DBC formed is weak (Table 2). By removing many of the acidic OH groups through methylation they are unable to form new chemical bonds, although some activation of the attached ring systems by methoxy substituents will be retained. The low σ_c values recorded can be interpreted as a consequence of the inhibition of the intermolecular bonding between particle surfaces. The second observation was that the paste produced on kneading was very moist indeed and consequently generates very little plastic strength. Methylated coal had lost most of its capacity to hold water in its pores presumably because of the reduction in H-bonds to oxygen groups in pore wall surfaces.

The decrease in crush strength maximum of the DBC (Figure 5) on extended drying we believe to be real and probably results from decreased H-bonding. This observation as well as those cited above are consistant with our hypothesis that cross-linking chemical reactions involving acidic hydroxyls and activated aromatised ring systems are involved in the development of microdomains between coal particles. They are also primarily involved in the development of the macrodomain strength in addition to compaction as a physical process and H-bonding by the residual water molecules, some of which will occupy pore space in the macrodomains.

Victorian brown coals can be fractionated into Solvent

Soluble Extracts (SSE), Humic Acids (HA) and a Kerogen (K) residue (6). These are lithotype dependent in concentration hence ROM coals will be variable also in the relative composition of functional groups reactive in densification. SSE have high H/C ratios (7) but do contain some acidic components. These latter could be involved in domain development but on first principles HA and K fractions may be expected to provide good substrates for cross-linking. Indeed humic acids have been implicated in the formation of Solar Dried Coal (8). In our tests neither HA or K additives enhanced the crush strengths derived from LY DBC. The complication of pH, as yet unresolved, clouds the interpretation however, since HA additives are acidic in nature and lower the pH of the raw coal feed. Low pH coals do not develop a significant crush strength in general, nor in the particular, as shown in Table 2 for Loy Yang coal.

Table 2. Effects of Kerogen and Humic Acid Additives on Densification.

Coal	Additive	pH	Crush Strength (MPa)
Loy Yang ROM	None	3.9	6.8
	25% Kerogen	4.3	8.3
	$NaHCO_3$	4.9	16.1
	20% Humic acid	3.5	5.8
	20% HA + NaOH	5.9	18.1

Densification offers an advantage in that it readily allows the formation of a moulded coal but importantly the gross characteristics of DBC are still those of the ROM coal (Table 2). Figure 7 exemplifies this well in that the pyrograms for Loy Yang ROM and DBC are very similar. Thermal desorption of brown coal at 350°C releases primarily triterpenoid components which are virtually lacking in the 600°C pyrogram. Thermal desorption of DBC with a base additive, however, gives a significantly lowered yield of triterpenoids and suggests that components can be chemically incorporated into the DBC by this process, once again implicating oxygenated functional groups in densification.

Acknowledgement.
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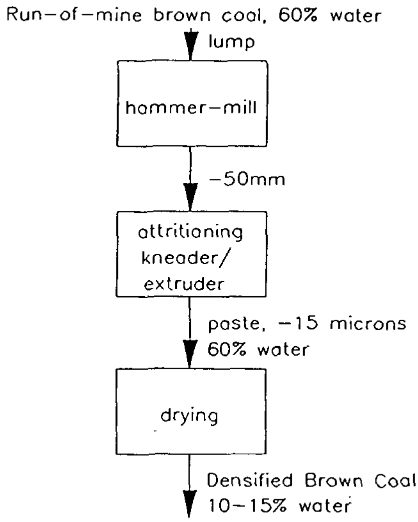
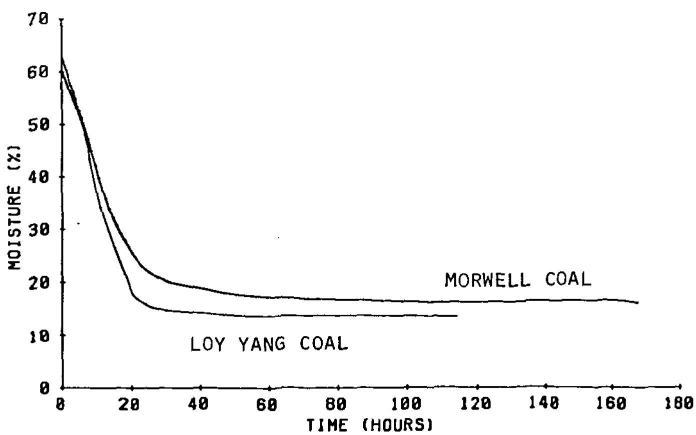
FLOW CHART FOR DENSIFICATION FIGURE 2



MOISTURE LOSS CURVES FIGURE 3

DRYING AT 20° C AND 50% REL. HUMID.



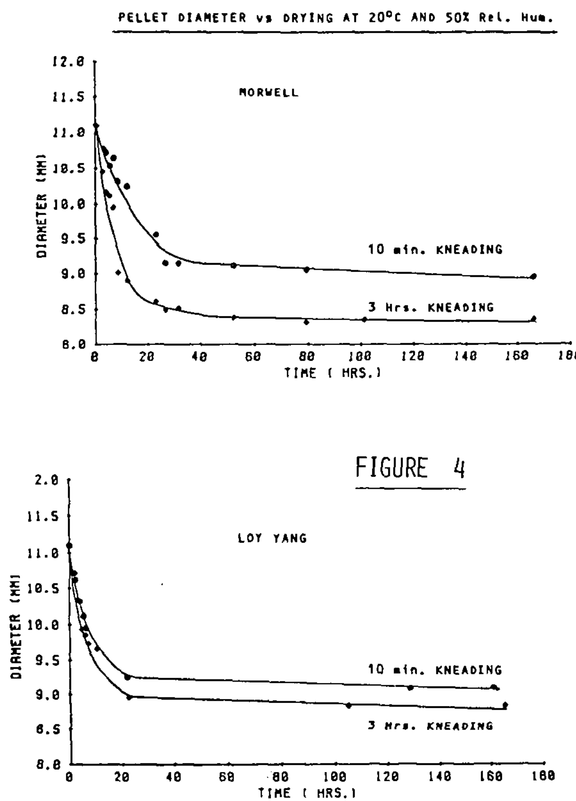


FIGURE 4

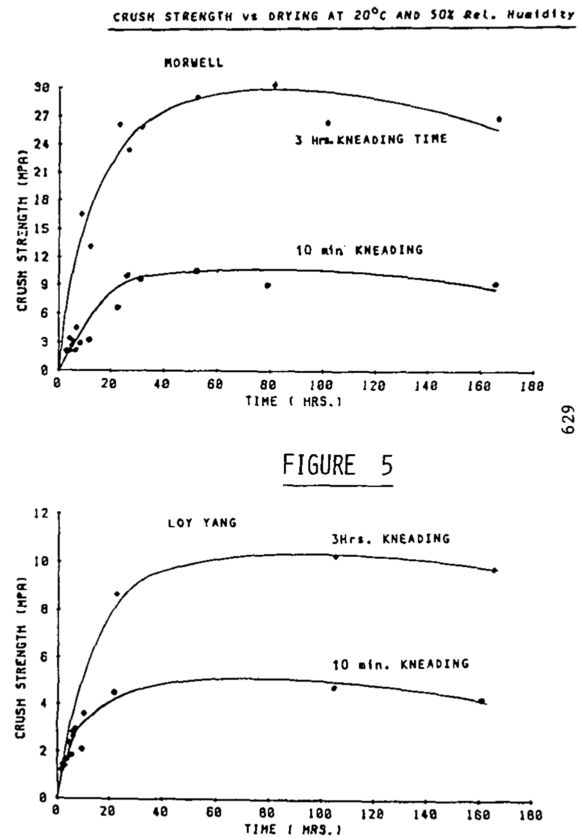
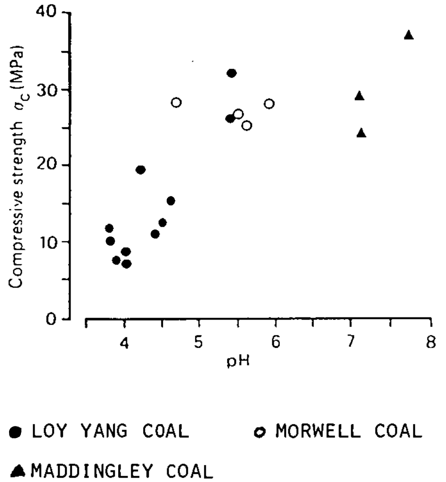


FIGURE 5



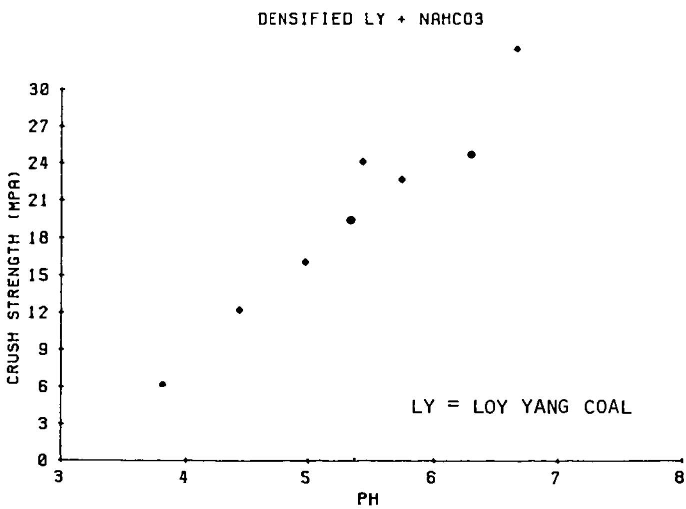


FIGURE 6. TYPICAL PH EFFECTS ON CRUSH STRENGTH

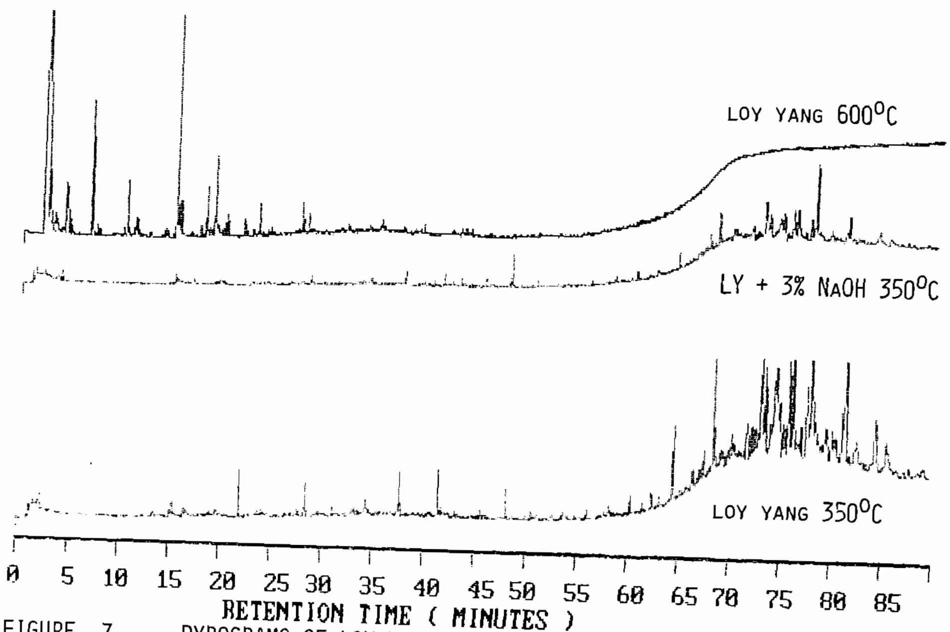


FIGURE 7. PYROGRAMS OF LOY YANG DENSIFIED COALS